

# PATENT SPECIFICATION

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## Process for regenerating Raney nickle and Raney cobalt catalysts.

### COMPLETE SPECIFICATION

We, STAMICARBON N.V., a Dutch limited liability company of 2 van der Maesenstraat, Heerlen, the Netherlands do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the regeneration of contaminated Raney nickel and Raney cobalt catalysts.

It is a known fact that a Raney nickel catalyst which has become practically inactive through its use in chemical processes, can be worked up to fresh catalyst by dissolving it in nitric acid, evaporating the resulting solution to dryness and converting the nickel salt into oxide by heating, subsequently processing the oxide to a nickel-aluminium alloy by means of aluminium. By far the greater part of the aluminium is removed from the nickel-aluminium alloy by reaction with alkali hydroxide, and after washing with water the Raney nickel catalyst is obtained.

According to the present invention either a Raney nickel catalyst or a Raney cobalt catalyst which has lost activity in a chemical process can be regenerated by treating the catalyst with a 0.5 — 5 N solution of an alkali metal hydroxide in water and/or in an alcohol miscible with water, and adding hydrogen or a metal which reacts with the hydroxide with evolution of hydrogen.

Any alkali metal hydroxide may be used in carrying out the invention; solutions of sodium or potassium hydroxide give good results and are readily available. Water or alcohols miscible with water may be used as solvents, e.g., methanol, ethanol, ethylene glycol and glycerin. Also mono-alkyl ethers of polyvalent alcohols, such as ethylene glycol mono-ethyl ether, and mono-alkyl ethers of glycerin, miscible with water, are suitable solvents.

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The process may be performed at room temperature or elevated temperatures. By preference a temperature of from 40 to 150°C is used, in which temperature range regeneration is faster and there is no advantage in using temperatures, above 150°C, and it is not desirable in practice because if the temperature is above the boiling point of the solution, the regeneration has to be carried out under pressure, e.g., 5—50 atm. requiring additional plant.

In carrying out the regeneration process according to the invention hydrogen may be conducted through the suspension of contaminated catalyst in the metal hydroxide solution; if elevated pressures are used, hydrogen may be passed into the suspension under pressure.

According to a preferred way of carrying out the invention the necessary hydrogen is evolved *in situ* by reaction of the hydroxide used with an added metal, preferably aluminium.

The catalyst may be easily separated from the hydroxide solution, e.g., by filtration. The removed catalyst may be freed from adhering solution by washing it with the solvent used. When water is used in the last washing a wet catalyst is obtained which may be kept in that state.

A catalyst may be subjected to repeated regeneration treatments according to the invention. However, if the catalyst is completely poisoned, e.g., by sulphur compounds, dissolution and renewed preparation of the catalyst has to be resorted to.

#### Example 1

100 grammes of a spent Raney nickel catalyst, containing 50% by weight of water, was suspended in  $\frac{1}{2}$  litre of a 4 N aqueous solution of sodium hydroxide and the suspension was heated for 2 hours at 100°C. while hydrogen was being passed through (at the rate of 1 litre per hour). Subsequently the catalyst was filtered and washed with

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water at room temperature until the washing water showed a neutral reaction.

- The catalyst was tested in the hydrogenation of phenol. The time needed for hydrogenation with the spent catalyst was four times as long as that needed for carrying out the process with the aid of the original catalyst, whereas with the aid of the regenerated catalyst the phenol hydrogenation was completed in the same time as with the original catalyst.

#### Example 2

- 300 grammes of a spent Raney cobalt catalyst suspension containing 150 grammes of water, was suspended in 2 litres of a 3 N aqueous solution of potassium hydroxide and heated for 2.5 hours at 100°C. During the heating process as suspension of 7.5 grammes of aluminium powder in 40 grammes of ethanol was gradually added.

- After cooling down to room temperature the catalyst — which had meanwhile settled — was separated from the liquid on top by decantation and then stirred in oxygen-free water. Decanting and stirring were repeated several times until the liquid showed a neutral reaction.

- A hydrogenation test proved that the original activity of the catalyst had been restored.

#### Example 3

- In a cylindrical pressure vessel with a capacity of 2 litres, 167 grammes of a catalyst paste, containing 40% by weight of cyclohexanol and 60% by weight of a spent Raney nickel catalyst used in the hydrogenation of phenol, was suspended in 1 litre of a 4 N aqueous solution of sodium hydroxide and 0.1 litre of ethanol.

- After the air had been removed, the pressure in the autoclave was raised to 10 atm. by forcing in hydrogen, and subsequently the contents were heated to 90°C. and stirred for two hours.

- After cooling down to room temperature the catalyst was separated from the solution and then washed in the manner described in example 2.

- In this way the activity of the catalyst was improved to 80% of its original value.

#### Example 4

- An amount of 100 kg of an inactive catalyst mass, obtained in the purification of caprolactam by a treatment with hydrogen in the presence of Raney nickel catalyst, which mass contained 40 kg of an aqueous solution of capro lactum (lactum content 20% by weight), was stirred in 500 litres of an aqueous solution containing 12% of sodium hydroxide. While hydrogen was being passed through at the rate of 900 litres per hour (measured at 0°C and 1 atm.), stirring was carried on for 2 hours at 80°C. During stirring a suspension of 2.5 kg of aluminium powder in 8 kg of ethanol was

gradually added.

The regenerated catalyst, separated off by decanting and washing with water, was suitable for use in the purification of caprolactam.

#### Example 5

50 grammes of a spent Raney cobalt catalyst was suspended in  $\frac{1}{2}$  litre of a 2 N solution of potassium hydroxide in methanol. The suspension was heated for 2 hours at 68°C under reflux, while hydrogen was being passed through at the rate of 2 litres per hour.

The solution of hydroxide in methanol was removed by decantation and the catalyst was washed with water. The catalyst regenerated in this way was again suitable for use in hydrogenations.

#### Example 6.

50 grammes of a spent hydrogenation catalyst (Raney nickel) was suspended in a solution of 40 grammes of sodium hydroxide in  $\frac{1}{2}$  litre of ethylene glycol containing 10% by weight of water. The suspension was heated at 80°C. for 2 hours while hydrogen was being passed through (1.5 litres per hour).

Subsequently the liquid was removed by decantation and the catalyst washed with water until the water showed a neutral reaction.

The regenerated catalyst was suitable as a hydrogenation catalyst.

#### Example 7

The regeneration according to example 6 was repeated with another amount of 50 grammes of the same catalyst, while instead of ethylene glycol  $\frac{1}{2}$  litre of glycerol monoethyl ether was used.

The catalyst purified in this way was again suitable as a hydrogenation catalyst.

#### WHAT WE CLAIM IS:—

1. A process for regenerating a Raney nickel catalyst or Raney cobalt catalyst, which has lost activity in a chemical process, the said regeneration comprising treating the spent catalyst with a 0.5—5 N solution of an alkali metal hydroxide in water and/or in an alcohol miscible with water, and adding hydrogen or a metal which reacts with the hydroxide with evolution of hydrogen.

2. A process according to claim 1, wherein hydrogen is evolved *in situ* by reacting the hydroxide with an added metal, preferably aluminium.

3. A process according to claim 1 or 2, carried out at a temperature of from 40 to 150°C.

4. A process for regenerating a Raney

nickel catalyst or a Raney cobalt catalyst substantially as described in any one of the specific examples herein.

- 5 A Raney nickel catalyst or a Raney cobalt catalyst when regenerated according to the process claimed in any one of the claims 1—4.

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